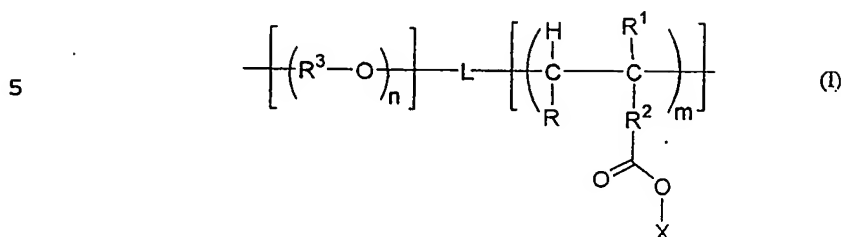


CLAIMS

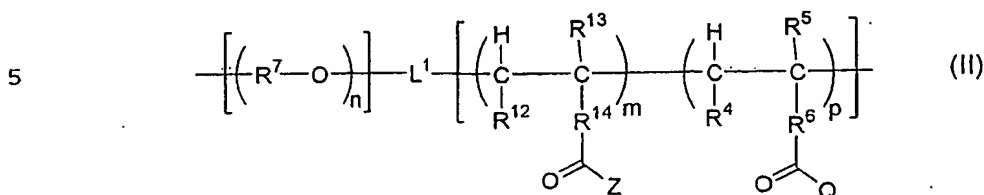
1. A block copolymer comprising the unit (I)



- 10 wherein R is selected from the group consisting of hydrogen, C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl, C₆-C₁₈ aryl, carboxylic acid, C₂-C₁₈ alkoxy carbonyl, C₂-C₁₈ alkaminocarbonyl, or any one of C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl, C₆-C₁₈ aryl, C₂-C₁₈ alkoxy carbonyl and C₂-C₁₈ alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R¹ is selected from the group consisting of hydrogen and C₁-C₆ alkyl groups; R² is a linking group; X is an electron withdrawing group; R³ is selected from the group consisting of C₁-C₁₈ alkylene, C₂-C₁₈ alkenylene, C₇-C₁₈ aralkylene, C₇-C₁₈ alkarylene and C₆-C₁₈ arylene; L is a divalent linker joining the blocks; and m and n are each an integer of greater than 1.
- 20 2. A block copolymer according to claim 1 in which m and n are integers of 5 to 300, more preferably 10 to 200, most preferably 25 to 150.
3. A block copolymer according to claim 1 or claim 2 which has a polydispersity of less than 1.4, preferably less than 1.2 and a molecular weight (Mw) of less than 100,000.
- 25 4. A block copolymer according to any preceding claim which is water soluble.
5. A block copolymer according to any preceding claim in which X is a carboxylate activating group, and is preferably selected from the group consisting of N-succinimidyl, pentachlorophenyl, pentafluorophenyl, para-nitrophenyl, dinitrophenyl, N-phthalimido, norbornyl, cyanomethyl, N-pyridyl, 30 N-trichlorotriazine, 5-chloroquinilino, and N-imidazole, more preferably an N-succinimidyl or imidazole moiety.

6. A block copolymer according to any preceding claim in which R is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₁-C₆ alkenyl, C₁-C₆ aralkyl and C₁-C₆ alkaryl; C₂-C₈ alkoxy carbonyl, C₂-C₈ alkaminocarbonyl, preferably hydrogen and methyl.
- 5 7. A block copolymer according to any preceding claim in which R¹ is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, pentyl or isomers thereof, preferably hydrogen and methyl.
8. A block copolymer according to any preceding claim in which R² is a bond or a divalent group selected from a carbonyl, C₁-C₁₈ alkylene and/or C₆-C₁₈ arylene group which may be substituted with 1 or more heteroatoms.
- 10 9. A block copolymer according to claim 8 in which R² is selected from the group consisting of C₁-C₆ alkylene, C₆-C₁₂ arylene, C₁-C₁₂ oxyalkylene and carbonyl-C₁-C₆ alkylene.
10. A block copolymer according to claim 9 in which R² is methylene, 1,2-ethylene, 1,3-propylene, hexylene, octylene, benzylene, tolylene or xylylene.
- 15 11. A block copolymer according to any preceding claim in which the groups R³, which may be the same or different, are selected from the group consisting of C₁-C₈ alkylene groups, preferably 1,2-alkylene, and C₆-C₁₂ arylene groups, most preferably methylene, ethylene, 1,2-propylene and 1,3-propylene.
- 20 12. A block copolymer according to claim 11 in which all R³ groups are the same and are preferably all 1, 2-ethylene or 1,2-propylene.
13. A block copolymer according to any preceding claim in which L comprises a C₁-C₁₈ alkylene or C₆-C₁₈ arylene group which may be substituted and/or interrupted with 1 or more heteroatoms.
- 25 14. A block copolymer according to claim 13 in which L is selected from the group consisting of C₁-C₆ alkylene, C₆-C₁₂ arylene, C₁-C₁₂ oxyalkylene and C₁-C₆ acyl.
15. A block copolymer according to claim 14 in which L comprises a COR^a group, wherein R^a is selected from the group consisting of C₁-C₆ alkylene or C₆-C₁₂ arylene, preferably methylene, 1,2-ethylene, 1,2-propylene, 1,3-propylene, ^{tert}butylene and ^{sec}butylene.
- 30

16. A block copolymer according to claim 1 which comprises the structure (II)



- wherein R^4 is selected from the group consisting of hydrogen, C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_7 - C_{18} aralkyl, C_7 - C_{18} alkaryl, C_6 - C_{18} aryl, carboxylic acid, C_2 - C_{18} alkoxycarbonyl, C_2 - C_{18} alkaminocarbonyl, or any one of C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_7 - C_{18} aralkyl, C_7 - C_{18} alkaryl, C_6 - C_{18} aryl, C_2 - C_{18} alkoxycarbonyl, and C_2 - C_{18} alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R^5 is selected from the group consisting of hydrogen and C_1 - C_6 alkyl groups; R^6 is a linking group; Q is a solubilising group selected from the group consisting of hydroxyl, C_1 - C_{12} alkyl, C_2 - C_{12} alkenyl, C_7 - C_{12} aralkyl, C_7 - C_{12} alkaryl, C_1 - C_{12} alkoxy, C_1 - C_{12} hydroxyalkyl, C_1 - C_{12} alkylamino, C_1 - C_{12} hydroxyalkylamino, or any of C_1 - C_{12} alkyl, C_2 - C_{12} alkenyl, C_7 - C_{12} aralkyl, C_7 - C_{12} alkaryl, C_1 - C_{12} alkoxy, C_1 - C_{12} hydroxyalkyl, C_1 - C_{12} alkylamino, C_1 - C_{12} alkylamino substituted with an amine, hydroxyl, carbonyl or thiol group; R^7 is selected from the group consisting of C_1 - C_{18} alkylene, C_2 - C_{18} alkenylene, C_7 - C_{18} aralkylene, C_7 - C_{18} alkylene and C_6 - C_{18} arylene; n, m and p are each an integer of greater than 1; R^{12} is selected from the group consisting of hydrogen, C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_7 - C_{18} aralkyl, C_7 - C_{18} alkaryl, C_6 - C_{18} aryl, carboxylic acid, C_2 - C_{18} alkoxycarbonyl, C_2 - C_{18} alkaminocarbonyl, or any one of C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_7 - C_{18} aralkyl, C_7 - C_{18} alkaryl, C_6 - C_{18} aryl, C_2 - C_{18} alkoxycarbonyl, and C_2 - C_{18} alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R^{13} is selected from the group consisting of hydrogen and C_1 - C_6 alkyl groups; R^{14} is a linking group; L^1 is a divalent linker joining the blocks; Z is a pendent group selected from the group consisting of $OM_{1/d}^{d+}$, NR^8R^9 , SR^{10} , OR^{11} and OX , wherein X is defined above, M is a metal ion and

d is an integer of 1 or 2, R⁸ comprises an alkyl group, preferably an aminoacyl substituted alkyl group, more preferably oligopeptidyl group; R⁹ is selected from hydrogen, C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl; R¹⁰ and R¹¹ comprise a group which is individually selected from the group consisting of hydrogen, C₁-C₁₂ alkyl, C₂-C₁₂ alkenyl, C₇-C₁₂ aralkyl, C₇-C₁₂ alkaryl and C₁-C₁₂ hydroxyalkyl, and may contain one or more cleavable bonds and may comprise a bioactive agent.

17. A block copolymer according to claim 16 in which Z comprises one or more aminoacyl groups, preferably 2-6 aminoacyl groups, most preferably 4 aminoacyl groups.

18. A block copolymer according to claim 17 in which Z comprises a glycine-leucine-phenylalanine-glycine linker.

19. A block copolymer according to claim 16 in which Z comprises a cis-aconityl group.

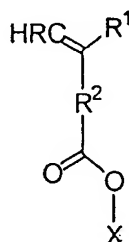
20. A block copolymer according to any of claims 16 to 19 in which Z comprises a bioactive agent or linker.

21. A block copolymer according to claim 20 in which the bioactive agent is selected from anti-cancer agents.

22. A block copolymer according to any of claims 16 to 21 in which Q comprises an amine group attached to the R⁶CO carbonyl carbon, preferably a C₁-C₁₂ hydroxyalkylamino group, most preferably a 2-hydroxypropylamino group.

23. A process for the production of a block copolymer, comprising the polymerisation of ethylenically unsaturated monomers including a compound

(III)

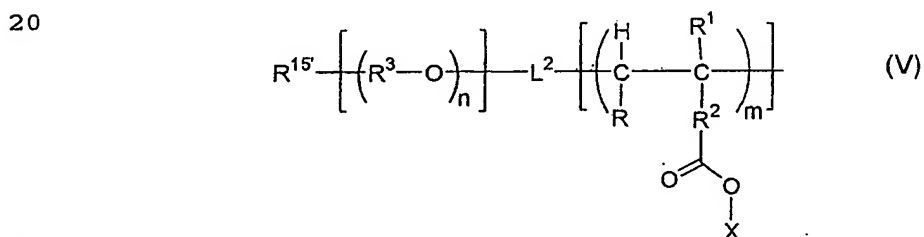


(III)

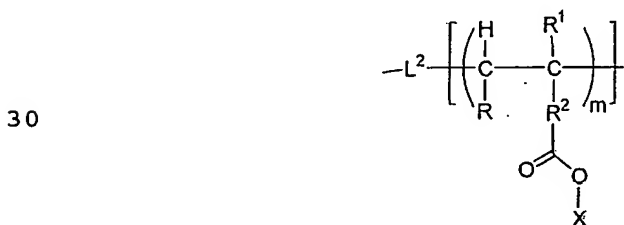
wherein R is selected from the group consisting of hydrogen, C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl, C₆-C₁₈ aryl, carboxylic acid, C₂-C₁₈ alkoxy carbonyl, C₂-C₁₈ alkaminocarbonyl, or any one of C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl, C₆-C₁₈ aryl, C₂-C₁₈ alkoxy carbonyl, and C₂-C₁₈ alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R¹ is selected from the group consisting of hydrogen and C₁-C₆ alkyl groups; R² is a linking group; X is an electron withdrawing group; in the presence of an initiator compound (IV)



wherein n is an integer of 1 or more and Y is a radical initiating group; R³ is selected from the group consisting of C₇-C₁₈ alkylene, C₂-C₁₈ alkenylene, C₇-C₁₈ aralkylene, C₇-C₁₈ alkarylene and C₆-C₁₈ arylene; R¹⁵ comprises a group selected from the group consisting of hydrogen, C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl and C₆-C₁₈ aryl, C₁-C₁₈ alkoxy, C₂-C₁₈ alkenyloxy, C₇-C₁₈ aralkoxy, C₇-C₁₈ alkaryloxy, C₆-C₁₈ aryloxy and -O-Y; to produce a block copolymer comprising the unit (V)



wherein m and n are as defined above and L² is a divalent linking group derived from Y and R^{15'} is R¹⁵, or where R¹⁵ is -O-Y, R¹⁵ is



24. A process according to claim 23 in which the groups X, R, R¹, R² and R³ are as defined in any of claims 2 to 15.

25. A process according to claim 23 or 24 in which Y is a -COR^y group, wherein R^y is selected from the group consisting of halogen substituted C₁-C₆ alkyl or C₆-C₁₂ aryl, preferably methyl, ethyl, propyl, ^{tert}butyl and ^{sec}butyl preferably CO^{tert}butylbromide.

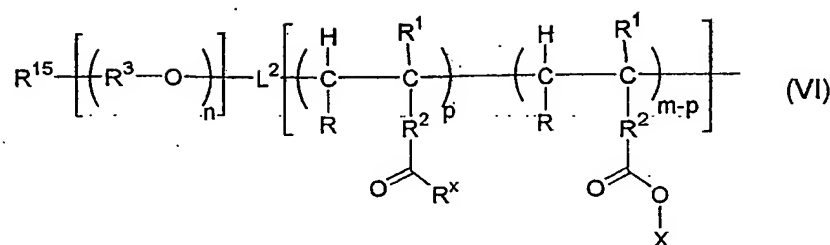
26. A process according to any of claims 23 to 25 in which L² is selected from the group consisting of C₁-C₆ alkylene, C₆-C₁₂ arylene, C₁-C₁₂ oxyalkylene and carbonyl-C₁-C₆ alkylene, preferably a -COR^a group, wherein R^a is selected from the group consisting of C₁-C₆ alkylene or C₆-C₁₂ arylene, preferably methylene, 1,2-ethylene, 1,2-propylene, 1,3-propylene, ^{tert}butylene and ^{sec}butylene.

27. A process according to any of claims 23 to 26 in which R¹⁵ is selected from hydrogen, C₁-C₆ alkyl, C₁-C₆ alkoxy, C₂-C₁₀ alkenyl, C₇-C₁₀ aralkyl, C₇-C₁₀ alkaryl and C₆-C₁₀ aryl and -O-Y, preferably methoxy or OY.

28. A process according to any of claims 23 to 27 which is a controlled radical polymerisation process, preferably an atom transfer radical polymerisation process, more preferably carried out in the presence of a polymerisation mediator comprising a Cu(I) complex.

29. A process according to any of claims 23 to 28 in which comonomers are copolymerised with the monomer of the formula III.

30. A process according to any of claims 23 to 29 in which the block copolymer of the formula V is reacted further with a reagent HR^x, wherein R^x is selected from the group consisting of NR¹⁹R²⁰, SR²¹ and OR²², wherein R¹⁹ is or comprises a linker group, preferably a substituted alkyl group, more preferably a peptidic group; R²⁰ is selected from hydrogen, C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl, C₆-C₁₈ aryl; R²¹ and R²² are selected from the group consisting of hydrogen, C₁-C₁₂ alkyl, C₁-C₁₂ alkenyl, C₁-C₁₂ aralkyl, C₁-C₁₂ alkaryl, C₁-C₁₂ alkoxy and C₁-C₁₂ hydroxyalkyl, any of which may comprise a bioactive agent substituent and/or may contain one or more cleavable bonds, to form a derivatised block copolymer having the structure (VI)

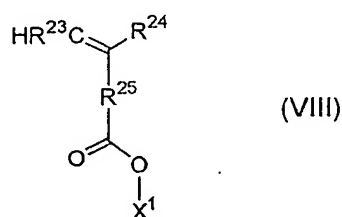


wherein $1 \leq p \leq m$.

31. A process according to claim 30 in which HR^x is H_2NR^2 in which R^2 comprises an aminoacyl linker or a cis-aconityl linker and a bioactive agent or a ligand.

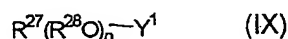
32.. A process according to claim 30 or 31 in which the block copolymer of the formula VI is quenched by reacting remaining groups -COOX with an amine-group-containing compound, preferably hydroxypropylamine.

33. A process for the production of a block copolymer, comprising the steps of (39) polymerising ethylenically unsaturated monomers comprising a compound (VIII)

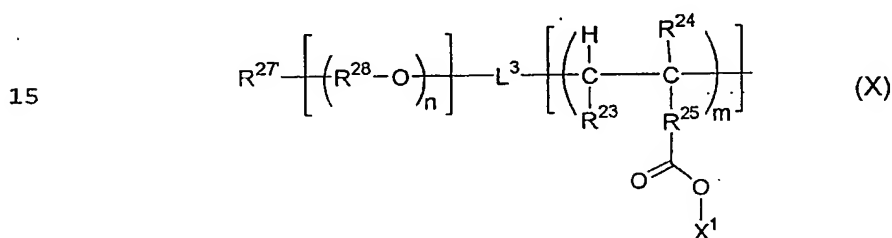


wherein R²³ is selected from the group consisting of hydrogen, C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl, C₆-C₁₈ aryl, carboxylic acid, C₂-C₁₈ alkoxy carbonyl, C₂-C₁₈ alkaminocarbonyl, or any one of C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl, C₆-C₁₈ aryl, C₂-C₁₈ alkoxy carbonyl, and C₂-C₁₈ alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R²⁴ is selected from the group consisting of hydrogen and C₁-C₆ alkyl groups; R²⁵ is a linking group; X¹ is selected from the group consisting of carboxyl activating groups, hydrogen, M¹_{1/d}^{d+} and carboxyl protecting groups, wherein M¹ is a metal ion and d is an integer of 1 or 2; R²⁶ is selected from the group consisting of C₁-C₁₈ alkylene,

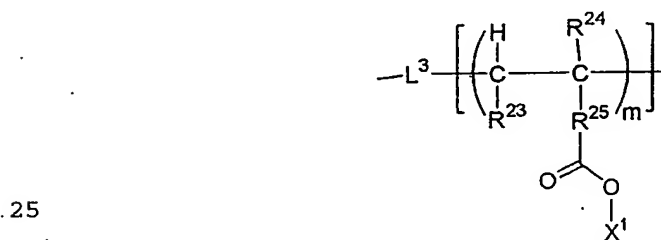
C₂-C₁₈ alkenylene, C₇-C₁₈ aralkylene, C₇-C₁₈ alkarylene and C₆-C₁₈ arylen; in the presence of an initiator compound (VIII)



5 wherein n is an integer of 1 or more and Y¹ is a radical initiating group, R²⁷ comprises a group selected from the group consisting of hydrogen, C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl and C₆-C₁₈ aryl, C₁-C₁₈ alkoxy, C₂-C₁₈ alkenyloxy, C₇-C₁₈ aralkoxy, C₇-C₁₈ alkaryloxy, C₆-C₁₈ aryloxy
 10 and -O-Y¹; and R²⁸ is selected from the group consisting of C₁-C₁₈ alkylene, C₂-C₁₈ alkenylene, C₇-C₁₈ aralkylene, C₇-C₁₈ alkarylene and C₆-C₁₈ arylen; to produce a block copolymer comprising the unit (X)

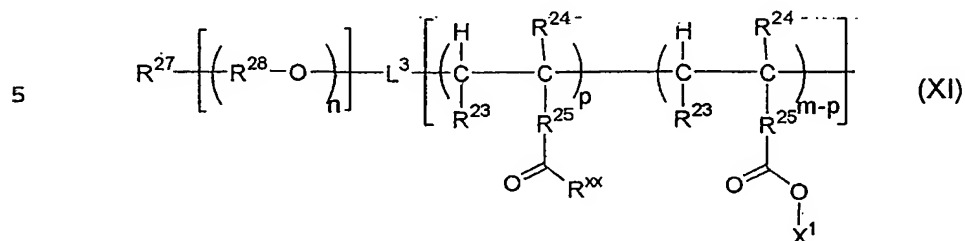


20 wherein m is an integer of greater than 1 and L³ is a divalent linking group derived from L³; and R²⁷ is R²⁷, or where R²⁷ is -O-Y¹, R²⁷ is



39. reacting (X) with a reagent HR^{xx}, wherein R^{xx} is selected from the group consisting of NR²⁹R³⁰, SR³¹ and OR³², wherein R²⁹ is a linker group, preferably a peptidic group; R³⁰ is selected from hydrogen, C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₇-C₁₈ aralkyl, C₇-C₁₈ alkaryl, C₆-C₁₈ aryl; R³¹ and R³² are
 30 individually selected from the group consisting of hydrogen, C₁-C₁₂ alkyl, C₁-C₁₂ alkenyl, C₁-C₁₂ aralkyl, C₁-C₁₂ alkaryl, C₁-C₁₂ alkoxy and C₁-C₁₂

hydroxyalkyl, and may contain one or more cleavable bonds, to form a derivatised block copolymer having the structure (XI)

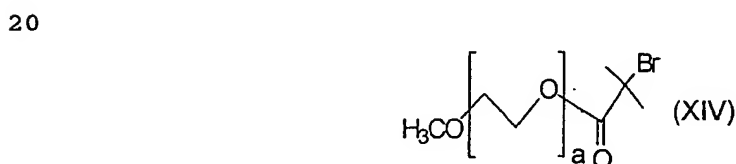


10 wherein $1 \leq p \leq m$.

34. A process according to claim 23 or claim 33 in which the ethylenically unsaturated monomer compound is

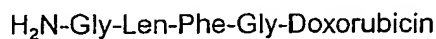


and the initiator is



25 in which a is 1 to 500.

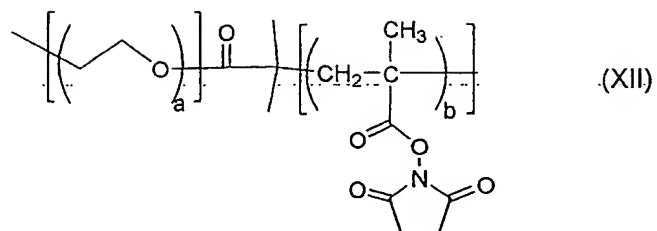
35. A process according to claim 34 in which the copolymer is reacted with a compound



and in which the product is reacted with 2-hydroxy-propylamine.

30 36. A block copolymer according to any of claims 1 to 22 having the structure (XII)

40



wherein a and b are integers of up to 500.

37. A block copolymer which is obtainable by reacting the block
 10 copolymer of claim 36 and a reagent selected to provide a pendant group
 comprising an aminoacyl linker or a cis-aconityl linker and a bioactive agent.